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Influence of Draining and Excluded Volume on the Translational Diffusion Coefficient of Flexible Polymers

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ABSTRACT: The mean translational diffusion coefficient for linear flexible polymers at infinite dilution is calculated with the two-parameter model, the Kirkwood approximation, and the renormalization group (RG) method. Calculations are performed to first order in $\epsilon = 4 - d$, where d is the spatial dimensionality, and describe the variation of the diffusion coefficient with draining and excluded volume. In the absence of RG calculations for the intrinsic viscosity, we investigate the qualitative effects of draining on the intrinsic viscosity by using the Weill–des Cloizeaux relation ($\alpha_\eta^3 \approx \alpha_H \alpha_S^2$) in conjunction with the RG calculations for α_H and α_S. The theory indicates that the commonly observed nonuniversality between the hydrodynamic (α_η and α_H) and static (α_S) expansion factor is likely due to the draining effect. As a consequence we conclude that the effect of draining may be quite substantial in good solvents even for very long polymers, and draining effects should be more carefully investigated theoretically and experimentally.

I. Introduction

The diffusion coefficient is widely used to characterize the molecular configuration of polymers at infinite dilution. Dynamical quantities such as the diffusion coefficient and intrinsic viscosity have the advantages that they may be measured easily and accurately. The disadvantage is that there is still no adequate theory to describe the hydrodynamic properties of long flexible linear polymers even in Θ solvents at infinite dilution. There are, however, moderately accurate approximate theories for unperturbed chains such as the Zimm theory and its modifications[1-3] that are applicable to very long chains under the preaveraging approximation. It would be desirable to have theories of similar accuracy that describe at least qualitatively the excluded volume and draining effects on dynamical properties.

Kirkwood[4] gives an approximate expression for the translational diffusion coefficient D of a linear flexible polymer at infinite dilution in the limit of zero shear rate as the simple equilibrium average

$$D = (k_B T/n\hat{\zeta})[1 + (\hat{\zeta}/6\pi\eta_s n)\sum_{i}\sum_{\substack{j \\ i\neq j}} \langle |\mathbf{R}_{ij}|^{-1} \rangle] \quad (1.1)$$

where $\hat{\zeta}$ is the friction coefficient of a monomer that is treated as a point-like friction source, n is the number of Kuhn units of length l, η_s is the solvent viscosity, and $k_B T$ is the absolute temperature in energy units.

By using the Fourier representation[5] of $|\mathbf{R}_{ij}|^{-1}$ we establish a connection between the double-sum term in (1.1) and the internal scattering function $S(k)$ whose excluded volume dependence is available from the work of Ohta et al.[6] Their $S(k)$, which is obtained by renormalization group (RG) methods, is then used to calculate (1.1) directly in the crossover regime. RG ideas are also used to analytically continue the results to describe the dependence of D upon draining. The investigation of these draining effects is one of the main purposes of this paper.

There are two approaches to evaluating (1.1) using the renormalization group (RG) method. The explicit average $\sum_{i\neq j}\langle |\mathbf{R}_{ij}|^{-1} \rangle$ can be calculated by exploiting its relation, mentioned above, to the internal scattering function. Alternatively, this average can be determined by analytically continuing the Oseen tensor via the Navier–Stokes equation in d dimensions and by evaluating the average of the d-space Oseen tensor again using the d-dimensional $S(k)$. An exact calculation for $d = 3$ must give the same result in both cases; however, approximate calculations differ between the two methods since the RG method employs the quantity $\epsilon = 4 - d$ as a perturbative parameter and since the perturbation expansion is truncated to finite order. This leads to differences between the two equally acceptable approaches.[7]

The dynamical RG method,[8] applied by Kawasaki and Shiwa[9] and Oono and Kohmoto,[10] uses the d-space Oseen tensor and has the advantage that the corrections to preaveraging may be described when the calculation is performed to second or higher order in ϵ. However, the calculations to date are only correct to first order in ϵ, although parts of the second-order contributions are included in the final expressions which are compared to experiment.[6,10] It remains to be determined how important are the contributions from the currently unknown second-order portions of the renormalization constants. However, Oono suggests on the basis of these calculations that the effect of preaveraging for the intrinsic viscosity is qualitatively similar to the results obtained by Zimm[2] and Garcia de la Torre.[13] It is notable that Oono and Kohmoto find no preaveraging error for the hydrodynamic radius, while Zimm and Garcia de la Torre observe it to have a preaveraging error (see Appendix B) even larger than that for the intrinsic viscosity. Perhaps a full second-order RG calculation may remove this discrepancy over the magnitude of the preaveraging approximation of the long-time diffusion coefficient using the Kirkwood equation (1.1).

We use the first method based on the $|\mathbf{R}_{ij}|^{-1}$ for all d because it is much simpler to apply, and only a first-order RG calculation is then required. Preaveraging approximations have been very useful in treating Gaussian chains, so their investigation with the rigorous RG methods probe their utility for describing polymer dynamics with excluded volume. We find here that the preaveraging RG approach in the poor and good solvent limits, respectively, produces

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results that are very similar to those obtained formerly from the two-parameter and blob models. For instance, in the limit of a non-free-draining Gaussian chain the classical expression for D given in Yamakawa[2] is obtained for $d = 3$. On the other hand, the relation between the classical expression for D and the dynamical RG result of Oono and Kohmoto[10] for a non-free-draining Gaussian chain is currently not evident. There is, thus, ample reason for pursuing both kinds of RG methods since each approximation has its own merits.

In section II the model is briefly described. An RG expression for the hydrodynamic radius is derived in section III, and RG ideas are used to incorporate draining effects in addition to the full excluded volume dependence. The ratio R_G/R_H, where R_G is the radius of gyration, is given in section IV, and a factor is introduced to correct R_H for the preaveraging approximation and to bring this ratio into accord with experiment. Draining effects on the intrinsic viscosity expansion factor are considered using the Weill–des Cloizeaux approximation.[14] Section VI describes the relation between the draining parameter and the hydrodynamic radius. Also we discuss theoretically the constancy of the product $\alpha_\eta h^*$ observed by Osaki et al.[15] Section VII gives a comparison between theory and experiment.

Elsewhere[16] the intrinsic viscosity and hydrodynamic expansion factors are derived under nondraining conditions in the preaveraging approximation without the use of the Weill–des Cloizeaux approximation. These results show the Weill–des Cloizeaux approximation to be about 10% in error, compared with Oono's[10] recent estimate of 5%. An error of similar magnitude is suggested to arise from the first-order ϵ-expansion procedure. The combination of the ϵ-expanded expressions for α_H and α_S and the Weill–des Cloizeaux relation leads to an accurate (within 4% in the nondraining limit) expression for α_η^3 due, in part, to some cancellation of errors. In section VIII the effect of draining is discussed qualitatively.

It is often presumed that the draining effect in long flexible macromolecules is negligible. Substantial evidence exists that long chains in the Θ state[2,17] and near-Θ state are nondraining, but deviations have been observed in good solvents.[17,18] In the past this last regime has been neglected since there had been no theory capable of describing it.

The most obvious physical implication of the RG theory for dynamical quantities (either the version of Oono and Kohmoto[10] or ours) is that the existence of nondraining requires the proportionality of α_H, α_η, and α_S for long polymers in a good solvent. In the classical experimental studies of Fujita et al.[19] and Noda et al.[20,21] this relation is observed and the proportionality constants are in good agreement with our nondraining theoretical expressions given in section VII. On the other hand, we find data that indicates the absence of a simple proportionality between these expansion factors in good solvents.[23] In some cases the departure is dramatic.[17,18]

Recently, a simplistic explanation of this widely observed phenomenon has been given by Weill and des Cloizeaux,[14] who argue, using the blob model, that the effect is due to a "spatial crossover". According to our RG calculations the blob model is incapable of adequately describing the crossover regime[16] and should not be considered for this purpose. Further our RG calculations indicate that the sometimes observed nonuniversal relation between the static and hydrodynamic expansion factors is probably due to draining.

II. Model

The same model is used for the excluded volume interaction as in the two-parameter (TP) theory.[2] The chain backbone is taken to be Gaussian, and the excluded volume is represented in terms of an idealized δ-function repulsive interaction. Such a model is restricted to the calculation of long-wavelength properties, where the detailed nature of the interaction potential is unimportant. Most TP calculations begin with a discrete bead-type model but ultimately pass to a continuum limit by replacing sums by integrals. We prefer to begin with a continuous version of the model. The model Hamiltonian of the configurational partition function is written as[22]

$$\frac{\mathcal{H}_a(\mathbf{R})}{k_BT} = \frac{d}{2l}\int_0^{N_0} d\tau \left|\frac{d\mathbf{R}(\tau)}{d\tau}\right|^2 + \frac{\beta_0}{2l^2}\int_0^{N_0} d\tau \int_0^{N_0} d\tau'\, \delta[\mathbf{R}(\tau) - \mathbf{R}(\tau')], \qquad |\tau - \tau'| \geq a \quad (2.1)$$

where $\mathbf{R}(\tau)$ designates the spatial position vector at a contour length τ along the chain, N_0 is the model variable corresponding to the chain length, a is a cutoff that prevents the self-interaction of the segments, k_BT is the absolute temperature in energy units, and d is the dimensionality of space, which is treated as a continuous variable, $d \in (2, 4)$.

It is convenient to rewrite eq 2.1 for computational simplicity as[8]

$$\frac{\mathcal{H}_a(\mathbf{c})}{k_BT} = \frac{1}{2}\int_0^{N_0} d\tau \left|\frac{d\mathbf{c}(\tau)}{d\tau}\right|^2 + \frac{\tilde{v}_0}{2}\int_0^{N_0} d\tau \int_0^{N_0} d\tau'\, \delta[\mathbf{c}(\tau) - \mathbf{c}(\tau')], \qquad |\tau - \tau'| \geq a \quad (2.2)$$

where the configurational coordinate and "bare excluded volume" are redefined as

$$\mathbf{c}(\tau) = (d/l)^{1/2}\mathbf{R}(\tau)$$

$$\tilde{v}_0 = (\beta_0/l^2)(d/l)^{d/2}$$

$$v_0 = \tilde{v}_0/(2\pi)^2 \quad (2.3a)$$

Using dimensional analysis, we introduce a dimensionless coupling constant u_0

$$v_0 = u_0\Lambda^{-\epsilon/2} \quad (2.3b)$$

where Λ is treated as a phenomenological scale characterizing some range of the excluded volume interaction along the chain.[16]

The actual polymer chain differs enormously from the model (2.1) over short length scales. The real chain is composed of molecular units with fixed bond lengths and is characterized by hindered rotations and complicated solvent-mediated interactions. The TP model, on the other hand, describes a continuous chain of zero thickness with a weakly repulsive δ-function interaction. It is quite clear that such a model is inadequate for the description of small-scale properties, but if we confine our attention to very large-scale properties, such as the radius of gyration, then the detailed nature of the small-scale interactions can be expected to be unimportant. We must, however, exercise some caution when using this model for properties that are more sensitive to shorter scales.

One strong motivation for the introduction of the RG methods is that the ordinary analytic version of the TP theory is an asymptotic expansion in $v_0N_0^{\epsilon/2}$ with $\epsilon = 4 - d$, and this expansion is of limited usefulness without modification. Lattice versions of the theory appear to be accurate, but it is desirable to obtain an analytic theory that is free of numerical uncertainties. The desired goal is to obtain an analytic theory starting with the well-known

TP model (without introducing any unwarranted assumptions) that accurately describes large-scale polymer properties even when the strength of the excluded volume interaction is large. The RG is a method to systematically resum the asymptotic expansion in $v_0 N_0^{\epsilon/2}$ based on an analysis of the analytic structure of large-scale polymer properties as a function of v_0, N_0, and d.

The resummation of the asymptotic TP theory is brought about by reparameterizing the theory in conjunction with a general scaling analysis. Part of this procedure involves the introduction of multiplicative renormalization constants Z_A which are defined to absorb divergences that arise when taking the sequence of limits $a \to 0$ and $\epsilon \to 0$ [see (2.2)]. Thus for any generic property, we have the relation between a bare unrenormalized quantity A_B and its renormalized analogue A

$$A = Z_A^{\pm 1} A_B$$

$$Z_A = 1 + \sum_{n=1}^{\infty} a_n u^n \tag{2.4}$$

The variable u is a small dimensionless expansion parameter which is defined through the "renormalization" of the dimensionless coupling constant u_0 [see (2.3b)]

$$u_0 = Z_u u$$

$$v = u\Lambda^{-\epsilon/2} \tag{2.5}$$

where $u = \tilde{u}/(2\pi)^2$ in analogy with (2.3a). A detailed description of the computational procedure and a heuristic discussion are given by Kholodenko and Freed.[24]

The model of hydrodynamic interaction is also an idealized one and therefore restricted to the description of large-scale properties. The polymer is considered to be a collection of beads with point sources of friction, connected by elastic entropic "springs", and the solvent is treated as a continuous fluid. The hydrodynamic interaction between the polymer segments is described by the Oseen tensor.[25] The Kirkwood approximation for D (the long-time diffusion coefficient at infinite dilution) introduces a preaveraging of the Oseen tensor to simplify its determination.

We do not discuss the full machinery of the chain conformational space RG method since the point of departure for our calculation is the already renormalized static-coherent-scattering function $S(k)$ given by Oono et al.[6] The derivation of the diffusion coefficient from (1.1) simply requires an extension of their calculation, so a description of the RG approach is unnecessary.

III. Kirkwood's Approximation Translational Diffusion Coefficient for a Linear Polymer and RG Analytic Continuation To Include Draining Dependence

Many workers have defined the dynamical radius by the expression

$$R_D^{-1} = \frac{1}{n^2} \sum_{\substack{i,j \\ i \neq j}} \langle |\mathbf{R}_{ij}|^{-1} \rangle \tag{3.1}$$

where $\langle \ldots \rangle$ denotes an equilibrium average. We could proceed to evaluate (3.1) directly for the physically pertinent situation of $d = 3$. However, it is useful to utilize the RG method in d space along with expansions in $\epsilon = 4 - d$. This approach aids us in performing the analytic continuation to generate expressions valid in the crossover domain between the good and poor solvent limits. A subsequent analytic continuation in subsection B below introduces the additional variation with the draining parameter.

We begin with the expression for the Fourier representation of $|\mathbf{r}|^{-1}$ in d space

$$\int |\mathbf{r}|^{-1} \exp(i\mathbf{k}\cdot\mathbf{r})\, d^d\mathbf{r} = F(k) = (2\pi^{1/2}/k)^{d-1}\Gamma[(d-1)/2] \tag{3.2}$$

where $d > 1$. The units of (2.3a) define $\mathbf{c}_{ij} = (d/l)^{1/2}\mathbf{R}_{ij}$. Then (3.1) may be written in a discrete notation as

$$R_D^{-1} = \left(\frac{d}{l}\right)^{1/2} \left\langle \sum_{\substack{i,j \\ i \neq j}} \int d^d\mathbf{k} \exp[-i\mathbf{k}\cdot(\mathbf{c}_i - \mathbf{c}_j)] F(k)/(2\pi)^d n^2 \right\rangle \tag{3.3}$$

where l is the Kuhn length of a statistical segment and $N = nl$ is the renormalized chain length. Passing to the continuous limit, the sums in (3.3) become integrals, and (3.3) is converted to

$$R_D^{-1} = \left(\frac{d}{l}\right)^{1/2} \int d^d\mathbf{k} \int_0^{N_0} d\tau \int_0^{N_0} d\tau' \times \langle \exp\{i\mathbf{k}\cdot[\mathbf{c}(\tau) - \mathbf{c}(\tau')]\}\rangle F(k)/(2\pi)^d, \qquad |\tau - \tau'| \geq a \tag{3.4}$$

From the definition of the static-coherent-scattering function $S_B(k,N_0,v_0)$ in (3.6) below, R_D^{-1} may be written in the form

$$R_D^{-1} = \left(\frac{d}{\pi l}\right)^{1/2} \{\Gamma[(d-1)/2]/\Gamma(d/2)\} \int_0^{\infty} \mathcal{J}(k,N,v,\Lambda) \tag{3.5}$$

where S_B is defined by[6]

$$S_B(k,N_0,v_0,a) = \int_0^{N_0} d\tau \int_0^{N_0} d\tau' \, \langle \exp\{i\mathbf{k}\cdot[\mathbf{c}(\tau) - \mathbf{c}(\tau')]\}\rangle \tag{3.6}$$

and $\mathcal{J}$ is the normalized scattering function

$$\mathcal{J}(k,N,v,\Lambda) = S_B(k,N_0,v_0,a)/S_B(0,N_0,v_0,a) = S(k,N,v,\Lambda)/S(0,N,v,\Lambda) \tag{3.7}$$

Here, S_B is the bare (unrenormalized) static-coherent-scattering function, while S is the renormalized quantity. Their explicit form is described in ref 6. It is only necessary to quote the renormalized S to first order[6] in $\epsilon = 4 - d$

$$S(k,N,u,\Lambda) = N^2\{S_0(\beta) - u[\mathcal{S}(\beta) \ln (2\pi N/\Lambda) + \bar{D}(\beta)] \tag{3.8a}$$

where $S_0(\beta)$, $\mathcal{S}(\beta)$, and $\bar{D}(\beta)$ are given by

$$S_0(\beta) = \beta^{-1} + \beta^{-2}(e^{-\beta} - 1), \qquad S_0(0) = \tfrac{1}{2} \tag{3.8b}$$

$$\mathcal{S}(\beta) = \beta^{-1}e^{-\beta} + \beta^{-2}(e^{-\beta} - 1), \qquad \mathcal{S}(0) = -\tfrac{1}{2} \tag{3.8c}$$

$$\bar{D}(\beta) = 2\int_0^1 dt \left\{ e^{-\beta}A(\beta - \beta t + \beta t^2) + (\beta^{-1} - \beta^{-2})A(-\beta t + \beta t^2) - \frac{[1 - \exp(-\beta t + \beta t^2)]}{\beta^2 t(1-t)} \right\} + \int_0^1 \left[\frac{1}{\beta(1-t)} + \frac{\exp(-\beta t + \beta t^2) - 1}{\beta^2} \right] - \beta^{-2}e^{-\beta}A(\beta) - \beta^{-1}e^{-\beta}[A(\beta) + 1], \qquad \bar{D}(0) = -\tfrac{1}{2} \tag{3.8d}$$

$$A(x) = \int_0^x dt\, (e^t - 1)/t \tag{3.8e}$$

$$\beta = Nk^2/2 \tag{3.8f}$$

A. Renormalization Group Approximation for D in Preaveraging Approximation. Equations 3.5 and 3.7 and the definition of Kirkwood's equation (1.1) provide the expression for D in terms of the d-space scattering function as

$$D = \frac{k_B T}{n\hat{\zeta}}\{1 + \left(\frac{d}{l}\right)^{1/2}\frac{\hat{\zeta}}{3\pi^{3/2}\eta_s}\frac{\Gamma[(d-1)/2]}{\Gamma(d/2)2n}\frac{N^2}{S(k=0)}\left(\frac{n}{N}\right)^2 \times \int_0^\infty S(k,N,u,\Lambda)\, dk \quad (3.9)$$

The integral in (3.9) with (3.8) gives a triple integral which is nontrivial to evaluate. This integral $I = (n/N)^2\int_0^\infty S(k,N,u,L)\, dk$ is explicitly calculated in Appendix A to obtain to order ϵ

$$I = (2\pi n/l)^{1/2}(2n/3)\{1 + u[(1/2)\ln(2\pi N/\Lambda) + K_\phi]\} \quad (3.10)$$

where

$$K_\phi \equiv \left(-\frac{3}{4}\right)\left\{\left[\frac{136(3^{1/2}) - 349}{72} - \frac{1}{24}\right]\pi + \frac{1496}{315} - \left(\frac{14 + 12\ln 2}{9}\right)\right\} \quad (3.11a)$$

$$K_\phi = 2.108$$

Equation 3.8 gives in the $k = 0$ limit ($k = |\mathbf{k}|$)

$$S(0,N,u,\Lambda)/N^2 = (1/2)[1 + u\ln(2\pi N/\Lambda) + 1] \quad (3.11b)$$

Substituting (3.10) and (3.11) into (3.9) transforms the latter into

$$D = (k_B T/n\hat{\zeta})\left[1 + \frac{2\hat{\zeta}(2dn)^{1/2}}{9\pi\eta_s l}\frac{\Gamma[(d-1)/2]}{\Gamma(d/2)}\mathcal{O}(N,u,\Lambda)\right] \quad (3.12a)$$

where to first order in ϵ we obtain

$$\mathcal{O}(N,u,\Lambda) = 1 - u[(1/2)\ln(2\pi N/\Lambda) + (1 - K_\phi)] + \mathcal{O}(u^2) \quad (3.12b)$$

The renormalization group arguments for the dynamical radius in the preaveraging approximation are identical with those given for $\langle \mathbf{R}^2 \rangle$ by Oono and Freed[6] and Kholodenko and Freed[24] so they are not repeated here. We merely quote the results in first order

$$R_D^{-1} = [N(1-\bar{u})^{1/4}]^{1/2} f(\zeta) \quad (3.13)$$

where

$$\zeta = (2\pi N/\Lambda)^{\epsilon/2}\bar{u}(1-\bar{u})^{-1+\epsilon/8}$$

$$\bar{u} = u/u^* \qquad u = u^*\zeta/(1+\zeta) \qquad u^* = \epsilon/8 \quad (3.14)$$

The variable ζ describes the crossover between the Gaussian and self-avoiding walk (SAW) regimes and is treated as a phenomenological variable to be determined by comparison with experiment. The scaling function $f(\zeta)$ is computed by relating (3.13) and (3.12). In section VII this ζ variable is transformed to one akin to the empirical z parameter of the TP theory, thereby enabling the conversion of our ζ-representation crossover predictions to a form more familiar to experimentalists.

Substituting the first-order definition of u from (3.14) into (3.12b) gives

$$\mathcal{O}(N,u,\Lambda) = 1 - \frac{\epsilon}{8}\left(\frac{\zeta}{1+\zeta}\right)\left[\frac{1}{2}\ln\left(\frac{2\pi N}{\Lambda}\right) + (1 - K_\phi)\right] + \mathcal{O}(\epsilon^2) \quad (3.15)$$

The result of the RG analysis is rather straightforward in this case. It merely indicates that (3.15) is to be analytically continued to

$$\mathcal{O}(N,u,\Lambda) = \left(\frac{2\pi N}{\Lambda}\right)^{-(\epsilon/16)[\zeta/(1+\zeta)]}\left[1 + (K_\phi - 1)\frac{\epsilon}{8}\frac{\zeta}{1+\zeta}\right] + \mathcal{O}(\epsilon^2) \quad (3.16)$$

Thus, D may be written to order ϵ using (3.12) and (3.16) as

$$D = \frac{k_B T}{n\hat{\zeta}}\left\{1 + \frac{2\hat{\zeta}(2dn)^{1/2}\Gamma[(d-1)/2]}{9\pi\eta_s l\Gamma(d/2)}\left(\frac{2\pi N}{\Lambda}\right)^{-[2\nu(\zeta)-1]/2}\left[1 + (K_\phi - 1)\frac{\epsilon}{8}\frac{\zeta}{1+\zeta}\right] + \mathcal{O}(\epsilon^2)\right\} \quad (3.17a)$$

where $2\nu(\zeta) - 1 = \epsilon\zeta/8(1+\zeta) + \mathcal{O}(\epsilon^2)$. This result may be improved by using the second-order expression for $2\nu(\zeta) - 1$, which is given by Kholodenko and Freed[24] as

$$2\nu(\zeta) - 1 = \frac{\epsilon}{8}\frac{\zeta}{(1+\zeta)^{17\epsilon/32} + \zeta}\left(\frac{2\pi N}{\Lambda}\right)^{-(\epsilon/4)[1/(1+\zeta)]} + \frac{15}{4}\left(\frac{\epsilon}{8}\right)^2\frac{\zeta}{1+\zeta} \quad (3.17b)$$

and which may be approximately written

$$2\nu(\zeta) - 1 \approx \frac{\epsilon}{8}\frac{\zeta}{1+\zeta} + \frac{15}{4}\left(\frac{\epsilon}{8}\right)^2\left(\frac{\zeta}{1+\zeta}\right)^2 \quad (3.17c)$$

A full second-order RG preaveraging calculation would yield additional prefactor terms[24] in $(\epsilon/8)^2\zeta^2/(1+\zeta)^2$ and $(\epsilon/8)^2\zeta/(1+\zeta)$, but these coefficients are presently unknown. We obtain an approximate second-order expression by using the second-order exponent in (3.17) and by hoping the second-order contributions are relatively small[24] as they are for $\langle \mathbf{R}^2 \rangle$. This modification is essential since the first-order prediction for $2\nu - 1$ is in very poor agreement with experiment, and it would be pointless to try to compare the first-order expression with experiment in good solvents.

B. Excluded Volume Dependence of Draining Effect. The RG method generally utilizes an ϵ-expansion of the d-dependent terms $d^{1/2}\Gamma[(d-1)/2]/\Gamma(d/2)$. Performing this ϵ-expansion yields

$$\Gamma[(d-1)/2]d^{1/2}/\Gamma(d/2) = \pi^{1/2}[1 + (\ln 2 - 5/8)\epsilon + \mathcal{O}(\epsilon^2)] \quad (3.18)$$

so insertion of (3.18) and (3.15) into (3.17) provides the alternative $\mathcal{O}(\epsilon)$ expression for D

$$D = \frac{k_B T}{n\hat{\zeta}}(1+\xi)\left[1 + (\ln 2 - 5/8)\epsilon\frac{\xi}{1+\xi} - \frac{\epsilon}{16}\left(\frac{\xi}{1+\xi}\right)\left(\frac{\zeta}{1+\zeta}\right)\ln\left(\frac{2\pi N}{\Lambda}\right) + 1.11\frac{\epsilon}{8}\left(\frac{\xi}{1+\xi}\right)\left(\frac{\zeta}{1+\zeta}\right)\right] \quad (3.19)$$

where ξ is related to the draining parameter h^* through

$$\xi = 2\hat{\zeta}(2\pi n)^{1/2}/9\pi l\eta_s = (4\pi/3)(2/3)^{1/2}h, \qquad h = h^*n^{1/2} \tag{3.20}$$

From the definition of the hydrodynamic radius

$$D = k_BT/6\pi\eta_sR_H \tag{3.21}$$

it is expected that $R_H \sim N^\alpha$ and $D \sim N^{-\alpha}$ for N large, where α is an effective exponent that depends on both the draining strength and the excluded volume interaction. The only analytic continuation of (3.19) consistent with this expectation is to exponentiate the ln (N/L) terms of (3.19) as

$$1 - \frac{\epsilon}{16}\left(\frac{\xi}{1+\xi}\right)\left(\frac{\zeta}{1+\zeta}\right)\ln\left(\frac{2\pi N}{\Lambda}\right) = \left(\frac{2\pi N}{\Lambda}\right)^{-(\epsilon/16)[\xi/(1+\xi)][\zeta/(1+\zeta)]} + \mathcal{O}(\epsilon^2) \tag{3.22}$$

A similar type of continuation is used by Oono and Kohmoto in their dynamical RG calculations.[10]

The introduction of (3.22) into (3.19) produces a crossover expression for D as a function of both the hydrodynamic and excluded volume interactions

$$D = \frac{k_BT}{n\hat{\zeta}}\left[(1+\xi)\left(\frac{2\pi N}{\Lambda}\right)^{-[\xi/(1+\xi)][(2\nu(\zeta)-1)/2]}\left\{1 + \frac{\xi}{1+\xi}\left[(\ln 2 - 5/8) + \frac{1.11}{8}\frac{\zeta}{1+\zeta}\right]\epsilon\right\}\right] + \mathcal{O}(\epsilon^2) \tag{3.23}$$

Further using (3.18) to resum the (ln 2 − 5/8) terms gives

$$D(\xi,\zeta) = (8/n)^{1/2}\frac{k_BT}{9\pi l\eta_s}\left(\frac{\xi+1}{\xi}\right)\left(\frac{2\pi N}{\Lambda}\right)^{-[\xi/(1+\xi)][(2\nu(\zeta)-1)/2]} \times \frac{\Gamma\left[\frac{3}{2} - \left(\frac{\xi}{1+\xi}\right)\left(\frac{4-d}{2}\right)\right]\left[4 - \left(\frac{\xi}{1+\xi}\right)(4-d)\right]^{1/2}}{\Gamma\left[2 - \left(\frac{\xi}{1+\xi}\right)\left(\frac{4-d}{2}\right)\right]} \times \left[1 + \frac{1.11}{8}\left(\frac{\xi}{1+\xi}\right)\left(\frac{\zeta}{1+\zeta}\right)\epsilon\right] + \mathcal{O}(\epsilon^2) \tag{3.24}$$

This latter resummation from (3.18) implies that the well-known Gaussian chain limits are recovered[2]

$$D(\text{free draining}) = k_BT/n\hat{\zeta}, \qquad \xi \sim 0$$

$$D(\zeta = 0) = \frac{k_BT}{n\hat{\zeta}}\left\{1 + \frac{2\hat{\zeta}(2dn)^{1/2}\Gamma[(d-1)/2]}{9\pi\eta_s l\Gamma(d/2)}\right\}, \qquad \xi \lesssim 1 \tag{3.25a}$$

The $\xi \to \infty$ non-free-draining limit is obtained from both (3.17) and (3.24) as

$$D(\xi \to \infty,\zeta) = (8/n)^{1/2}\frac{k_BT}{9\pi l\eta_s}\frac{\Gamma[(d-1)/2]}{\Gamma(d/2)}d^{1/2}\left(\frac{2\pi N}{\Lambda}\right)^{-[(2\nu(\zeta)-1)/2]}\left(1 + \frac{1.11}{8}\epsilon\frac{\zeta}{1+\zeta}\right) + \mathcal{O}(\epsilon^2) \tag{3.25b}$$

The hydrodynamic radius is written using (3.21) and (3.24) as a function of ζ and ξ

$$R_H(\xi,\zeta) = \frac{3}{4}\left(\frac{\langle R^2\rangle_0}{2}\right)^{1/2}\left(\frac{\xi}{1+\xi}\right)\left(\frac{2\pi N}{\Lambda}\right)^{[\xi/(1+\xi)][(2\nu(\zeta)-1)/2]} \times H(\xi)\left[1 - \frac{1.11}{8}\left(\frac{\xi}{1+\xi}\right)\left(\frac{\zeta}{1+\zeta}\right)\epsilon\right] + \mathcal{O}(\epsilon^2) \tag{3.26}$$

$$H(\xi) = \Gamma[2 - \xi(4-d)/2(1+\xi)]/\Gamma[3/2 - \xi(4-d)/2(1+\xi)][4 - \xi(4-d)/(1+\xi)]^{1/2} \tag{3.27}$$

$$R_H(\text{free draining}) = n\hat{\zeta}/6\pi\eta_s \tag{3.28}$$

The dynamical radius R_D is defined to be free from the complications of draining. From (3.5) and (3.10) it is obtained as

$$R_D = \frac{3}{4}\frac{\Gamma(d/2)\langle\mathbf{R}^2\rangle_0^{1/2}}{(2d)^{1/2}\Gamma[(d-1)/2]}\left(\frac{2\pi N}{\Lambda}\right)^{[2\nu(\zeta)-1]/2}\left[1 - \frac{1.11}{8}\epsilon\frac{\zeta}{1+\zeta}\right] + \mathcal{O}(\epsilon^2) \tag{3.29}$$

where $R_D(\zeta) = R_H(\xi \to \infty,\zeta)$.

Above it is shown that our RG calculations reduce to those well-known results in the free-draining Gaussian chain limit. We also obtain the classical non-free-draining Gaussian chain limit

$$D(\zeta = 0, \xi \to \infty) = (8d/n)^{1/2}k_BT\Gamma[(d-1)/2]/9\pi l\eta_s\Gamma(d/2) \tag{3.30}$$

$$R_H(\zeta = 0, \xi \to \infty) = (3/4)(\langle\mathbf{R}^2\rangle_0/2d)^{1/2}\Gamma(d/2)/\Gamma[(d-1)/2] \tag{3.31}$$

in agreement with the results quoted in Yamakawa[2] for $d = 3$. More generally, the $\zeta \to 0$ limit of (3.24) produces a new expression for a partial draining Gaussian chain

$$D(\zeta = 0,\xi) = (8/n)^{1/2}(k_BT/9\pi\eta_s l)[(\xi+1)/\xi]H(\xi)^{-1} \tag{3.32}$$

$$R_H(\zeta = 0,\xi) = (3/4)(\langle\mathbf{R}^2\rangle_0/2)^{1/2}H(\xi)[\xi/(1+\xi)] \tag{3.33}$$

IV. Ratio of the Radius of Gyration to the Hydrodynamic Radius

Oono and Freed[6] provide the crossover expression for the radius of gyration as

$$R_G \equiv \langle\mathbf{S}^2\rangle^{1/2} = (\langle\mathbf{R}^2\rangle_0/6)^{1/2}\left(\frac{2\pi N}{\Lambda}\right)^{[2\nu(\zeta)-1]/2}\left(1 - \frac{13}{192}\epsilon\frac{\zeta}{1+\zeta}\right) + \mathcal{O}(\epsilon^2) \tag{4.1}$$

which may be combined with R_H in (3.26) to define the ratio

$$\mathcal{H}(\xi,\zeta) = R_H(\xi,\zeta)/R_G(\zeta) = \frac{3(3)^{1/2}}{4}\frac{\xi}{1+\xi}\left(\frac{2\pi N}{\Lambda}\right)^{-[1/(1+\xi)][(2\nu(\zeta)-1)/2]}H(\xi) \times \left(1 - \frac{1.11}{8}\left(\frac{\xi}{1+\xi}\right)\left(\frac{\zeta}{1+\zeta}\right)\epsilon + \frac{13}{192}\epsilon\frac{\zeta}{1+\zeta}\right] + \mathcal{O}(\epsilon^2) \tag{4.2}$$

There are two interesting limiting cases of $\mathcal{H}(\xi,\zeta)$ corresponding to non-free-draining chains and chains in good and Θ solvents ($d = 3$)

$$\mathcal{H}(\infty,0) = 3\pi^{1/2}/8 = 0.665 \tag{4.3a}$$

$$\mathcal{H}(\infty,\infty) = 0.929\mathcal{H}(\infty,0) = 0.618 \tag{4.3b}$$

Draining in the unperturbed state reduces the ratio $\mathcal{H}$, and an increase of the excluded volume interaction also de-

creases $\mathcal{H}$. The blob model[26,27] yields $\mathcal{H}_{blob}(\infty,\infty) = 0.538$, in qualitative agreement with our RG results.

Recent Monte Carlo calculations of Zimm[12] and by Garcia de la Torre et al.[13] show that there is an error due to preaveraging which is in accord with the experimentally observed error for calculated quantities such as the Flory factors Φ_0 ($[\eta]M = (6\langle S^2\rangle)^{3/2}\Phi$, where $[\eta]$ is the intrinsic viscosity) and P_0 ($f/\eta_s = P(6\langle S^2\rangle)^{1/2}$, where f is the friction coefficient and η_s is the solvent viscosity). The error is a function of n for small chains. Following the Monte Carlo data of Garcia de la Torre et al.,[13] we introduce an ad hoc correction factor $\lambda(n)$ for the hydrodynamic radius. The corrected hydrodynamic radius, R_H^c, is written as

$$R_H^c = \lambda(n)R_N(\text{Kirkwood}) \tag{4.4a}$$

$$\lambda(n) = 1/[0.86 + 0.25(n+1)^{-0.5}] \tag{4.4b}$$

For long chains this predicts that $\lambda(\infty) = 1.163$ and $\rho_0^c = 1/\mathcal{H}_0^c = 1.29$ where $\mathcal{H}_0^c = \lambda(\infty)\mathcal{H}(\infty,0)$. This is to be compared with the experimental value of $\rho_\Theta = 1.27 \pm 0.06$ obtained by Schmidt and Burchard,[28] $\rho_\Theta = 1.25$ obtained by Vrentas,[29] and $\rho_\Theta = 1.28 \pm 0.02$ obtained by Tsunashima, Nemoto, and Kurata.[30] Zimm's[12] Monte Carlo value is $\rho_0 = 1.28$. Alternatively λ may be introduced as a phenomenological correction factor following Vrentas.[29]

Assuming the error due to preaveraging is independent of excluded volume strength, there is a simple way of avoiding the inaccuracy due to preaveraging that does not require the introduction of correction factors. The dimensionless expansion coefficient should largely have the preaveraging effect cancel. The hydrodynamic expansion factor is from (3.26) [see section VIII]

$$\alpha_H = R_H/R_{H0} = (2\pi N/\Lambda)^{[\xi/(1+\xi)][(2\nu(\zeta)-1)/2]}\left[1 - \frac{1.11}{8}\left(\frac{\xi}{1+\xi}\right)\left(\frac{\zeta}{1+\zeta}\right)\epsilon\right] + \mathcal{O}(\epsilon^2) \tag{4.5}$$

V. Approximate Expression for the Intrinsic Viscosity

RG calculations for the intrinsic viscosity are not available in the equilibrium-averaged approach pursued here. Nor are two-parameter theory calculations of $[\eta]$ available as a function of draining parameter. If available, they could be used[16] to provide an approximate RG description of the simultaneous draining and excluded volume dependence of $[\eta]$. Since draining has been believed by some to be important for $[\eta]$ in good solutions and by others to be always unimportant, we utilize the Weill–des Cloizeaux approximation[14]

$$[\eta]_{W\text{-}C} \propto R_H R_G^2/M \tag{5.1}$$

where M is the molecular weight, as a *qualitative* tool to probe expected draining effects on $[\eta]$ before pursuing more elaborate partial draining, excluded volume dependent calculations of the polymer viscosity. If we regard (5.1) as a qualitatively useful formula, then crossover expressions for the intrinsic viscosity expansion factor follow from (4.1) and (4.5) as

$$\alpha_{\eta W\text{-}C}{}^3 = \left(\frac{2\pi N}{\Lambda}\right)^{[2\nu(\zeta)-1][1+\xi/2(1+\xi)]}\left(1 - \frac{13}{96}\epsilon\frac{\zeta}{1+\zeta}\right)\times\left[1 - \frac{1.11}{8}\epsilon\left(\frac{\zeta}{1+\zeta}\right)\left(\frac{\xi}{1+\xi}\right)\right] + \mathcal{O}(\epsilon^2) \tag{5.2}$$

It is noted that in the free-draining limit we have[20] $\alpha_\eta{}^3 = \alpha_S{}^2$ and in the good solvent regime (non-draining) $\alpha_\eta{}^3 \propto \alpha_S{}^3$. These results are compatible with the Weill–des Cloizeaux approximation [see section VIII]. The viscosity expansion factor α_η reduces for non-free-draining to

$$\alpha_{\eta W\text{-}C}{}^3(\xi \to \infty) = \left(\frac{2\pi N}{\Lambda}\right)^{3[2\nu(\zeta)-1]/2}\left(1 - \frac{13}{96}\epsilon\frac{\zeta}{1+\zeta}\right)\times\left(1 - \frac{1.11}{8}\epsilon\frac{\zeta}{1+\zeta}\right) + \mathcal{O}(\epsilon^2) \tag{5.3}$$

According to (5.2) $\alpha_\eta{}^3$ is completely insensitive to draining in the unperturbed state, but this is not necessarily so upon expansion [see section VIII]. Notice that if the term $[1 - 13\epsilon\zeta/96(1+\zeta)][1 - 1.11\epsilon\zeta/8(1+\zeta)]$ is expanded to first order, then we have $[1 - 0.274\epsilon\zeta/(1+\zeta)]$. In the limit $\zeta \to \infty$ these expressions differ by about 3%. This type of error arising from the ϵ-expansion is typical.

We introduce[2] the equations defining P and Φ for the general case when these depend on draining and excluded volume

$$f = (6\langle \mathbf{S}^2\rangle)^{1/2}P(\xi,\zeta) = 6\pi R_H\eta_s \tag{5.4}$$

$$[\eta]M = (6\langle \mathbf{S}^2\rangle)^{3/2}\Phi(\xi,\zeta) \tag{5.5}$$

Using the Weill and des Cloizeaux assumption (5.1) along with the RG predictions for $D = kT/f$ and $\langle \mathbf{S}^2\rangle$, the crossover expressions for $\Phi(\xi,\zeta)/\Phi(\xi,\zeta=0)$ and $P(\xi,\zeta)/P(\xi,\zeta=0)$ are found to be

$$P(\xi,\zeta)/P(\xi,\zeta=0) = \left(\frac{2\pi N}{\Lambda}\right)^{[-(1/(1+\xi))][(2\nu(\zeta)-1)/2]}\left(1 + \frac{13}{96}\epsilon\frac{\zeta}{1+\zeta}\right)\left[1 - \frac{1.11}{8}\left(\frac{\xi}{1+\xi}\right)\left(\frac{\zeta}{1+\zeta}\right)\epsilon\right] + \mathcal{O}(\epsilon^2) \tag{5.6}$$

$$P(\xi,\zeta)/P(\xi,\zeta=0) \approx \Phi(\xi,\zeta)/\Phi(\xi,\zeta=0) \tag{5.7}$$

Equation 5.7 is in qualitative agreement with the data for $\Phi(\zeta)/\Phi_0 = \Phi(\xi\to\infty,\zeta)/\Phi_0(\xi\to\infty)$ summarized in Norisuye et al.[19] and Noda et al.[21]

Tanaka[31] has strongly criticized the use of the Weill–des Cloizeaux approximation because it leads to the prediction (5.7) which "clearly conflicts with experiment". The experimental data he refers to is that of Noda et al.,[20] who find $P(\zeta)/P_0 = P(\xi\to\infty,\zeta)/P_0(\xi\to\infty)$ to be equal to unity within experimental uncertainty over the whole range of the excluded volume interaction. Data of Noda et al.[21] for $\Phi(\zeta)/\Phi_0$ suggest that the Weill–des Cloizeaux approximation incurs an error ranging from 0 to 10% upon going from a poor to good solvent.

There is not enough evidence, however, to establish the general phenomenological validity of $P/P_0 \approx 1$, which is in conflict with numerous other experimental and theoretical investigations. For example, ter Meer et al.[32] find instead that P/P_0 is about 0.8 in good solvents and Cowie and Bywater[22] observe P/P_0 to be a monotonically decreasing function with excluded volume. Pritchard and Caroline, Munch et al., and Vidakovic and Rondelez have also recently noted[33] that P/P_0 varies in a nonuniversal way with the radius of gyration expansion factor. We point out, however, that we still believe that Noda et al.'s conclusion that $P(\zeta)/P_0 \approx 1$ is correct for *nondraining* chains despite the extensive evidence that this relation is not in general true. The discrepancy, we believe, is due to the draining effect, which has formerly been neglected.

Theoretical calculations are also in disagreement with $P/P_0 \approx 1$. For example, in good solvents (an asterisk denotes an observable in a good solvent) eq 4.3 gives $P^*/P_0 = 0.93$, the blob model[27] ($\nu = 0.59$) and the related Peterlin

model[2] ($\epsilon = 2\nu - 1$) yield $P^*/P_0 = 0.82$ and 0.83, respectively, and the dynamical RG calculation[10] of Oono and Kohmoto implies $P^*/P_0 = 0.79$. Quite recently, Barrett[35] obtains $P^*/P_0 = 0.92$ from a lattice calculation based on (3.1). Thus if we accept $P/P_0 \approx 1$, then we must conclude that all of these expressions disagree with experiment by about 7–20%. The 10% errors of the Weill–des Cloizeaux approximation are thus reasonable given the apparent crudeness of available theory and experimental data for P/P_0. This approximation is quite adequate, at least, to describe the qualitative effects of draining on $\alpha_\eta{}^3$, an observable for which there are reliable data.

VI. Draining Parameter with Excluded Volume

The Kirkwood–Riseman theory in three dimensions with no excluded volume predicts the diffusion constant D to be[2]

$$D = (k_B T/n\hat{\zeta})(1 + 8(2)^{1/2}h_0/3) \tag{6.1}$$

where the draining parameter is

$$h_0 = \hat{\zeta}n^{1/2}/(12\pi^3)^{1/2}\eta_s l = h_0{}^* n^{1/2} \tag{6.2}$$

Equation 6.1 is now used to define the quantity $h(\zeta)$ for a theory with excluded volume

$$D \equiv (k_B T/n\hat{\zeta})[1 + 8(2)^{1/2}h(\zeta)/3] \tag{6.3}$$

By comparing (3.23), (3.29), and (6.1), $h(\zeta)$ is found to be

$$h(\zeta) = \frac{\hat{\zeta}d^{1/2}\Gamma[(d-1)/2](2\pi N/\Lambda)^{-[(2\nu(\zeta)-1)/2]}n^{1/2}}{12\pi\eta_s l\Gamma(d/2)}\left(1 + \frac{1.11}{8}\epsilon\frac{\zeta}{1+\zeta}\right) + \mathcal{O}(\epsilon^2) \tag{6.4}$$

with $h(\zeta) = h^*(\zeta)n^{1/2}$ and $h^*(d = 3, \zeta = 0) = h_0{}^*$. Other expressions for the draining parameters have been proposed before. For example, in the Zimm–Peterlin scheme [p 302 of ref 2], $h[\nu(z)]$ is given by

$$h(\nu) = [2^{\nu-1/2}/(12\pi^3)^{1/2}](\hat{\zeta}/\eta_s l)n^{-[(2\nu(z)-1)/2]}n^{1/2} \tag{6.5}$$

where $\nu(z) = (1/2)(\partial \ln \alpha_S{}^2/\partial \ln z)$ and the z is the well-known excluded volume parameter. Equation 6.4, based on the RG analysis, is similar to (6.5).

Osaki et al.[15] apply the bead–spring model to good solutions by empirically varying the hydrodynamic parameter h^* [defined analogously to (6.3)] to simulate excluded volume effects in good to moderate solutions. They thereby use this empirical h^*_{emp} to correlate, albeit in an ad hoc fashion, the effect of solvent power on the observed spectrum of viscoelastic relaxation times for linear polymers. Osaki et al.[15] observe that $\alpha_\eta h^*_{emp}$ is very insensitive to solvent condition, $\alpha_\eta h^*_{emp} = 0.21 \pm 0.02$. Our expressions for α_η in (5.2) and $h(\zeta)$ in (6.4) yield the product $\alpha_\eta h^*(\zeta)$ in three dimensions

$$\alpha_\eta h^*(\zeta) = \left(1 + 0.0472\frac{\zeta}{1+\zeta}\right)h_0{}^* \tag{6.6}$$

Since $h(\zeta)$ is proportional to the dynamical radius, eq (6.6) is really equivalent to

$$\alpha_\eta h^*(\zeta) = h_0{}^*\alpha_\eta/\alpha_D \tag{6.7}$$

whose relative constancy has been noted independently by Roovers and Toporowski[36] to hold for comb and star polymers as well. The identification of $h^*(\zeta)$ and h^*_{emp} is made on the assumption that in the low-frequency regime for very long polymers the Kirkwood–Riseman[2] theory and Kirkwood equation (1.1) give a good approximation to the diffusion coefficient calculated from the finite string bead–spring model used by Osaki et al.

Equation 6.6 indicates that $\alpha_\eta h^*_{emp}$ should not vary by more than 5% with a change in the molecular weight, solvent, or temperature. The observation that h^*_{emp} does not change for many polymers suggests that the value of h^*_{emp} for the linear chain is a universal constant having the value $h^*_{emp} \approx 0.21 \pm 0.02$. The theoretical treatment of the bead–spring model by Osaki[36] for finite nondraining linear chains predicts that $h_0{}^*$ is a universal constant, $h_0{}^*$(theory) = 0.25, in good agreement with the data of Osaki et al. When $h_0{}^*$(theory) is corrected for preaveraging [see (4.4)], we have $h_0{}^{*c}$(theory) = 0.22. The Flory constant Φ_0 is also observed to be insensitive to the molecular weight over a very large range.[2] In the Osaki theory (which assumes preaveraging) the value of Φ_0 is a constant if $h_0{}^*$(theory) = 0.25, and this is taken as further evidence that $h_0{}^*$(theory) $\simeq$ 0.25 for a Gaussian chain or equivalently that Gaussian chains are phenomenologically non-free-draining.

VII. Comparison with Experiment

The notation in which the RG results are presented is probably unfamiliar to most polymer scientists. There are many different equivalent representations of the RG predictions,[16] and one exists that is close to that used in the two-parameter theory. These expressions involve an empirical quantity $\bar{z}$ akin to z of the two-parameter theory where $\bar{z}$ is treated as a phenomenological variable.

The discussion of alternative representations of the RG theory is involved and is given elsewhere.[16] Here we only consider the results that are easily interpreted. To illustrate the notation, consider the radius of gyration expansion factor which we find to be in three dimensions

$$\alpha_S{}^2 = (1 + 32\bar{z}/3)^{1/4}(1 - 13\lambda_1/96)$$
$$\lambda_1 = (32\bar{z}/3)/(1 + 32\bar{z}/3), \qquad \bar{z} \le 0.15 \tag{7.1}$$
$$\alpha_S{}^2 = 1.71\bar{z}^{0.3672}, \qquad \bar{z} > 0.75 \tag{7.2}$$

where $\bar{z}(d = 3) = (3/4)u(2\pi N/\Lambda)^{\epsilon/2}$ and $(2\nu - 1) = [\epsilon/8 + (15/4)(\epsilon/8)^2 + \ldots]_{d=3} = 0.1836$. There is a more general expression for the regime $\bar{z} \in (0.15, 0.75)$, but (7.1) may be regarded as an approximate expression in this regime. The determination of $\bar{z}$ from experimental data is the same as that used by Miyaki and Fujita[37] and is discussed below.

The RG hydrodynamic radius (3.26) can be converted in this notation to

$$\alpha_H = (1 + 32\bar{z}/3)^{\xi/8(1+\xi)}[1 - 0.139\lambda_1\xi/(1+\xi)], \qquad \bar{z} \le 0.15 \tag{7.3}$$

$$\alpha_H = (6.441\bar{z})^{0.1836[\xi/(1+\xi)]}[1 - 0.139\xi/(1+\xi)], \qquad \bar{z} \ge 0.75 \tag{7.4}$$

which becomes in the non-free-draining limit

$$\alpha_H(\xi \to \infty) = \alpha_D = (1 + 32\bar{z}/3)^{1/8}[1 - 0.139\lambda_1], \qquad \bar{z} \le 0.15 \tag{7.5}$$
$$\alpha_H = 1.21\bar{z}^{0.1836}, \qquad \bar{z} \ge 0.75 \tag{7.6}$$

Using the Weill–des Cloizeaux approximation[14] (5.1), the $\bar{z}$ form of (4.1), (7.5), and (7.6) yields the viscosity expansion factor

$$\alpha_{\eta w\text{-}c}{}^3 \approx (1 + 32\bar{z}/3)^{1/4+\xi/8(1+\xi)}(1 + 0.135\lambda_1) \times [1 - 0.139\xi\lambda_1/(1+\xi)], \qquad \bar{z} \le 0.15 \tag{7.7}$$

$$\alpha_{\eta w\text{-}c}{}^3(\xi \to \infty) \approx (1 + 32\bar{z}/3)^{3/8}(1 - 0.135\lambda_1)(1 - 0.139\lambda_1), \qquad \bar{z} \le 0.15 \tag{7.8}$$

$$\alpha_\eta{}^3(\xi \to \infty) \approx 2.08\bar{z}^{0.5508}, \qquad \bar{z} \ge 0.075 \tag{7.9}$$

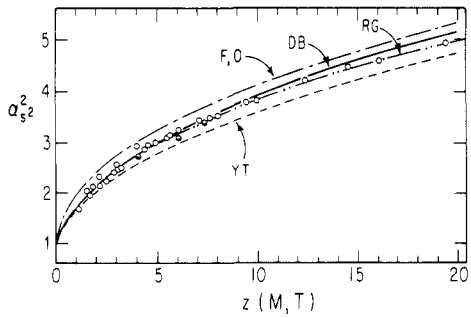

Figure 1. Relation between α_S^2 and the phenomenological excluded volume parameter $z(T,M) \propto \tau M^{1/2}$. The experimental data in the figure are reproduced from ref 28. Theoretical predictions are denoted by lines. The dashed curve is the Yamakawa–Tanaka equation,[2] the dot–dash curve is the Domb–Barrett equation,[2] the large and small dashed line is the "old" Flory equation, the double-dot–dashed line is our RG prediction in eq 7.1, and the solid line is the Domb–Barrett equation.[30] The large unfilled circles are for PS (polystyrene) in benzene; the bottom-half-filled circles are for PIB (polyisobutylene) in *n*-heptane.

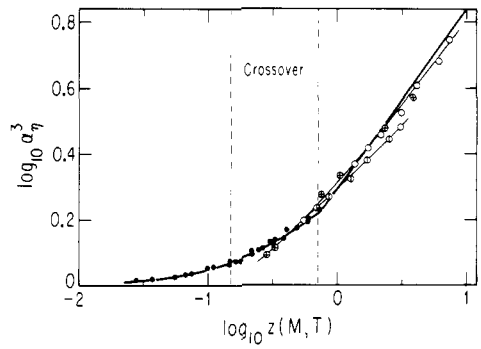

Figure 2. The large unfilled circles and the circles with a cross are for PIB in cyclohexane at 25 °C.[28] Those with a circle and a bar are for PIB in *n*-heptane at 25 °C; the small filled circles are for PIB in IAIV at different temperatures. Figure 2 is reproduced from ref 28 with our approximate expression for α_η^3 from eq 7.8 and 7.9 superimposed. The light lines are a best linear fit to data, and the vertical dashed lines denote the crossover regime $\bar{z} \in (0.15, 0.75)$.

In this approximation the ratio $\Phi(\xi \to \infty)/\Phi_0$ is obtained as

$$\Phi(\xi \to \infty)/\Phi_0 \approx 1 - 0.071\lambda_1, \qquad \bar{z} \leq 0.15 \quad (7.10)$$

It is important when making a comparison with experiment that the definition of the empirical z variable is self-consistent with the theoretical $\bar{z}$ variable theory. In the work of Miyaki and Fujita[37] z is determined by assuming validity of the Domb–Barrett equation,[38] which is numerically very similar to (7.1) and (7.2). They find z is accurately described by the phenomenological variable $z_{emp} = c\tau M^{1/2}$, where c is a constant, $\tau = (T - \Theta)/T$, and Θ is the theta temperature. To make the relation to our $\bar{z}$ we merely rescale the phenomenological z in their empirical $\alpha_S^2 - z_{emp}$ plot until the $\alpha_S^2 - z_{emp}$ and $\alpha_S^2 - \bar{z}_{theory}$ (RG) plots match in terms of a best fit. If the fit is very good as in the case of the data of Miyake and Fujita[37] and of Miyaki, Einaga, and Fujita,[39] then a reasonable comparison with experiment can be made.

Figure 1 presents our expression for $\alpha_S^2(\bar{z})$ along with the experimental data of Miyaki and Fujita where $\bar{z} = \mu z_{Fujita}$ and $\mu = 0.906$. The intrinsic viscosity expansion factor is plotted in Figure 2 against the same phenomenological z_{Fujita} as used in the radius of gyration factor in Figure 1. Substituting $\bar{z} = \mu z_{Fujita}$ into (7.8) and (7.9) gives α_η^3 in terms of $z_{Fujita} = z(T,M)$.

Our agreement with experiment may, however, be fortuitous in the case of α_η^3 and could be due to a cancellation of errors between the RG and Weill–des Cloizeaux approximations. In another paper[16] we show how the traditional TP theory calculations[2] may be converted approximately to the RG representation in terms of $\bar{z}$ where the expanded RG representation agrees with the TP calculations to first order[2] in $\bar{z}$. In this case we obtain for α_S^2, $\alpha_H(\xi \to \infty)$, and $\alpha_\eta^3(\xi \to \infty)$ the following:[16]

$$\alpha_S^2 = (1 + 32\bar{z}/3)^{1/4}(1 - 0.130\lambda_1), \qquad \bar{z} \leq 0.15$$
$$= 1 + 1.28\bar{z} + \mathcal{O}(\bar{z}^2) \quad (7.11)$$
$$\alpha_S^2 = 1.72\bar{z}^{0.3672}, \qquad \bar{z} \geq 0.75$$
$$\alpha_H(\xi \to \infty) = (1 + 32\bar{z}/3)^{1/8}(1 - 0.068\lambda_1), \qquad \bar{z} \leq 0.15$$
$$= 1 + 0.609\bar{z} + \mathcal{O}(\bar{z}^2) \quad (7.12)$$
$$\alpha_H(\xi \to \infty) = 1.31\bar{z}^{0.1836}, \qquad \bar{z} \to 0.75$$
$$\alpha_\eta^3(\xi \to \infty) = (1 + 32\bar{z}/3)^{3/8}(1 - 0.276\lambda_1), \qquad \bar{z} \leq 0.15$$
$$= 1 + 1.06\bar{z} + \mathcal{O}(\bar{z}^2) \quad (7.13)$$
$$\alpha_\eta^3(\xi \to \infty) = 2.02\bar{z}^{0.5508}, \qquad \bar{z} \geq 0.75$$

where the calculation of α_η^3 *does not* assume the Weill–des Cloizeaux approximation. It is noted that the RG expressions for α_S^2 and $\alpha_\eta^3(\zeta \to \infty)$ given in (7.1) to (7.9) are very close to the corresponding expressions (7.11) to (7.13). There is, however, a discrepancy between $\alpha_H(\xi \to \infty)$ as calculated directly from the ϵ-expansions (7.3) to (7.4) or from the combination of TP and RG theories in (5.9). Some experimental evidence by Noda et al.[21] indicates that $\alpha_S = \alpha_H(\xi \to \infty)$ to within experimental uncertainty, suggesting that the expression based on RG with the coefficient determined from the two-parameter calculation and the Kirkwood theory[2] (7.12) is more accurate than the ϵ-expansion RG calculation of this paper. The origin of this discrepancy is probably the ϵ-expansion procedure. It is a simple matter to correct the suspected error in (7.3) and (7.4) by replacing the prefactor coefficient –0.139 in these expressions by the more reliable value –0.068 from (7.12). The expansion factor $\alpha_\eta^3(\xi \to \infty)$ obtained from the Weill–des Cloizeaux approximation (7.8) to (7.9) may also be corrected, but in this case the correction is very small. These tiny refinements are really not relevant to the main issue we wish to consider—the *qualitative* effect of draining on hydrodynamic properties.

VIII. Draining

The draining effect adds a new dimension of complication to the description of dynamic properties. It is commonly observed that approximate theories for non-free-draining chains are in fair agreement with experiment for long flexible polymers in Θ solvents and it is often assumed that, since Θ chains display this behavior, the same should be true of swollen chains. The non-free-draining character of a Θ chain is not surprising since the polymer forms a relatively dense coil. However, upon expansion it is intuitively expected that the solvent begins to stream more through the outer sheath of the polymer, possibly producing a draining effect that should manifest itself by making the exponent σ of $\alpha_\eta^3 \sim M^\sigma$ less than $3(2\nu - 1)/2$ in good solvents. Here ν is the exponent for the radius of gyration, $\langle S^2 \rangle \propto M^{2\nu}$. It is commonly observed that $\sigma < 3(2\nu - 1)/2$ in good solvents, in agreement with our expectations, but the difficulty is how to theoretically account for it.

The draining and excluded volume interaction parameters cannot be taken as independent of each other on basic physical considerations. This is assumed in eq 4.5 implicitly in the definition of the hydrodynamic expansion factor. More properly, if we allow the draining parameter

of a Gaussian chain to be different from that of a swollen chain, we have

$$\alpha_H = \frac{[\xi/(1+\xi)]H(\xi)}{[\xi_0/(1+\xi_0)]H(\xi_0)}\left(\frac{2\pi N}{\Lambda}\right)^{(\xi/(1+\xi))[2\nu(\zeta)-1]/2}\left[1 - \frac{1.11}{8}\left(\frac{\xi}{1+\xi}\right)\left(\frac{\zeta}{1+\zeta}\right)\epsilon\right] + \mathcal{O}(\epsilon^2) \quad (8.1)$$

where $\xi_0 = \xi(\zeta = 0)$ is the draining parameter for an unperturbed chain.

A reasonable assumption may be introduced to simplify this expression. From the experimental observation of non-free-draining behavior for Gaussian coils we introduce the assumption $\xi_0 \to \infty$ to obtain

$$\alpha_H = [\xi/(1+\xi)]\frac{H(\xi)(4-\epsilon)^{1/2}\Gamma(2-\epsilon/2)}{\Gamma(3/2-\epsilon/2)}\left(\frac{2\pi N}{\Lambda}\right)^{(\xi/(1+\xi))[(2\nu(\zeta)-1/2]}\left[1 - \frac{1.11}{8}\left(\frac{\xi}{1+\xi}\right)\left(\frac{\zeta}{1+\zeta}\right)\epsilon\right] + \mathcal{O}(\epsilon^2) \quad (8.2)$$

We can then make some rough considerations concerning the phenomenological dependence of the draining parameter ξ and excluded volume parameter ζ. From the definition of these parameters in (3.14) and (3.20) both should be proportional to $M^{1/2}$ in three dimensions. Thus, an increase in the molecular weight should bring about an increase in the draining and excluded volume parameters.

In other paper[11] we show that ζ is proportional to the z parameter of the conventional two-parameter theory. As mentioned in the preceding section z is often taken to have the phenomenological dependence[40] $z \propto \tau M^{1/2}$ in three dimensions. It is reasonable to assume as a heuristic guess that the draining is inversely proportional to the strength of the interaction parameter β or $\xi \propto (1/\tau)M^{1/2}$. This assumption is in accord with the observed insensitivity of Gaussian chains to draining and the assumption $\xi_0 \to \infty$. It is noted that the sensitivity of a particular polymer to draining is dependent on the nonuniversal constant of proportionality.

Next, if we write (8.2) in the $\bar{z}$ notation and employ the Weill–des Cloizeaux approximation, we have equations (7.3), (7.4), and (7.7) with the extra draining factor

$$\mathcal{F}(\xi) = (\xi/(1+\xi))H(\xi)/H(\xi \to \infty) \quad (8.3)$$

The qualitative prediction, based on our assumed phenomenological dependence of ξ, is that non-free-draining would be observed in the near-Gaussian regime $\bar{z} \lesssim 0.15$ and in the excluded volume crossover regime $\bar{z} \in (0.15, 0.75)$ where the polymer is relatively dense and τ is small. For the good solvent regime $\bar{z} \gtrsim 0.75$, where the swelling of the coil first becomes substantial, a splitting in the α_η^3 vs. z plot is predicted where all phenomenological data for draining chains must lie below the asymptotic non-free-draining curve given by $\xi \to \infty$. The expected splitting pattern is apparent in Figure 2. Our naive description should be extended to a more quantitative one and is given only to be suggestive of a more precise description. This type of analysis offers great promise in elucidating the effect of draining on hydrodynamic properties.

IX. Conclusion

The theoretical description of hydrodynamic properties of long flexible linear polymers, even in the simplest case of infinite dilution and unperturbed chains, is inadequate, and only approximate theories are available. We give a theoretical expression for the hydrodynamic radius based on the Kirkwood equation (1.1) and a further RG motivated analytic continuation that does not assume the non-free-draining limit. The starting point of our calculation is the static-coherent-scattering function as obtained with the renormalization group in conjunction with the two-parameter model. Our results for the unperturbed state reduce to well-known expressions for free-draining and non-free-draining chains, so that our theory provides an extension of this approximate theory for Gaussian chains. New expressions are obtained that describe the crossover in the hydrodynamic and excluded volume interactions. It is stressed that this is done without introducing dynamical renormalization group methods and therefore at the expense of being confined to the preaveraging approximation.

We then apply our approximate expressions to discuss the constancy of $\alpha_\eta h^*$, where h^* is a phenomenological draining parameter in the finite string bead–spring model. In order to probe the draining dependence of α_η^3, we utilize an approximation due to Weill and des Cloizeaux to obtain a qualitatively correct RG expression for α_η^3. The observed splitting of the phenomenological α_η^3–z_{emp} plot of Miyaki and Fujita is also discussed in terms of the draining effect. It is found that the theoretical α_η^3–z_{emp} plot based on the Weill–des Cloizeaux approximation is in good agreement with experiment, and the small splitting in the α_η–z_{emp} plot is in qualitative accord with our theoretical expression that includes the effect of partial draining. Thus, although our calculations are approximate, they are capable of describing some of the essential features of the dependence of hydrodynamic properties on draining and the excluded volume interaction.

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Appendix A. Evaluation of the Integral (3.10)

Using the definitions of $S(k,N,u,L)$ and β given in (3.8), eq 3.10 is rewritten as

$$I = I_1 + I_2 - (n^2u)(I_3 + I_4 + I_5 + I_6) \quad (A.1)$$

where

$$I_1 = (n/N)^2\int_0^\infty N^2S_0(\beta)\,dk = \lim_{s\to 0}[n^2/(2nl)^{1/2}] \times \int_0^\infty \exp(-s\beta)[1/\beta^{3/2} + (e^{-\beta}-1)/\beta^{5/2}]\,d\beta = \frac{\pi^{1/2}(2n)^{3/2}}{3l^{1/2}} \quad (A.2)$$

$$I_2 = (n/N)^2\int_0^\infty -u\ln\left(\frac{2\pi N}{\Lambda}\right)\left[\frac{\partial}{\partial\beta}\mathcal{S}(\beta)\right] \times (2nl\beta)^{-1/2}\,d\beta = (\tilde{u}/3)(n/2\pi)^{3/2}l^{-1/2}\ln(2\pi N/\Lambda) \quad (A.3)$$

and the remaining integrals are subsequently considered. The whole integral (A.2) converges, but individual terms are undefined. The extra $\lim_{s\to 0}[\exp(-s\beta)]$ factor has been introduced to enable us to consider these individual terms separately and to use results from the theory of Laplace transforms. The third integral in (A.1) is

$$I_3 = 2\int_0^\infty\int_0^1\left\{\left(\frac{1}{\beta} - \frac{1}{\beta^2}\right)A(-\beta t + \beta t^2) - \left[\frac{1-\exp[t(1-t)]}{\beta^2 t(1-t)}\right]\right\}dt\,dk \quad (A.4)$$

Integrating (A.4) by parts with respect to k, interchanging the order integration, and letting $\alpha = \beta t(1-t)$ gives

$$I_3 = 2\int_0^1 \int_0^\infty \left\{\left[\frac{t(1-t)}{\alpha} - 1\right] t(1-2t) + \frac{t(1-t)}{\alpha}\right\}\left(\frac{e^{-\alpha}-1}{\alpha}\right)[2nl\alpha t(1-t)]^{-1/2}\, d\alpha\, dt$$

Using the same method of introducing $\lim_{s\to 0}[\exp(-st)]$ in I_1 yields

$$I_3 = (-17/24)\pi^{3/2}/(2nl)^{1/2} \qquad (A.5)$$

The integral I_4 is defined by

$$I_4 = 2\int_0^\infty \int_0^1 \beta^{-2} e^{-\beta} A(\beta - \beta t + \beta t^2)\, dt\, dk \qquad (A.6)$$

Upon integrating parts with respect to k and performing trivial integrations, it is converted to the form $I_4 = I_4' + I_4''$, where

$$I_4' = \int_0^1 \frac{t(1-2t)\{[t(1-t)]^{3/2} - [t(1-t)]^3\}}{[1-t(1-t)](2nl)^{1/2}}\, dt \qquad (A.7a)$$

$$I_4'' = 2\int_0^\infty [e^{-\beta} A(\beta)/\beta^{5/2}]\, d\beta \qquad (A.8)$$

The integral I_4' is best evaluated by splitting the interval (0, 1) in half and letting $u = 4t(1-t)$ to obtain

$$I_4' = [\pi^{1/2}/3(2nl)^{1/2}] \times \left\{8\int_0^1 \frac{u^{3/2}(1-u)^{1/2}}{u-4} - \frac{1}{8}\int_0^1 \frac{u^3(1-u)^{1/2}}{u-4}\, du\right\} \qquad (A.7b)$$

The first of these integrals is found by standard hypergeometric function recursion relations[41] to equal

$$\int_0^1 \frac{u^{3/2}(1-u)^{1/2}}{u-4}\, du = -\frac{1}{3}B(5/2, 3/2)\, {}_2F_1(1, 3/2; 4; -1/3) = -\frac{\pi}{48}[102(2-3^{1/2})^2 - 8(2-3^{1/2})]$$

The second hypergeometric integral is likewise evaluated and combined with the preceding to give

$$I_4' = (\pi/2nl)^{1/2}\left\{\frac{[136(3)^{1/2} - 349]\pi}{72} + \frac{1496}{315}\right\} \qquad (A.9)$$

I_5 is evaluated together with I_4'' as

$$I_4'' + I_5 = \int_0^\infty [e^{-\beta} A(\beta)/\beta^2 + e^{-\beta} A(\beta)/\beta + e^{-\beta}/\beta] \frac{d\beta}{(2nl\beta)^{1/2}} \qquad (A.10)$$

The terms in this integral are special cases of

$$J(\alpha) = (2nl)^{-1/2}\int_0^\infty e^{-\beta}\beta^{-\alpha} A(\beta)\, d\beta \qquad (A.11a)$$

We introduce the identity

$$\Gamma(\alpha)/2\beta^\alpha = \int_0^\infty e^{-\beta r^2} r^{2\alpha-1}\, dr \qquad (A.11b)$$

to convert $J(\alpha)$ into

$$J(\alpha) = [2/\Gamma(\alpha)]\int_0^\infty r^{2\alpha-1}\int_0^\infty e^{-(r^2+1)\beta} A(\beta)\, d\beta\, dr \qquad (A.11c)$$

Integrating by parts with respect to β and using the definition of the Laplace transform gives

$$J(\alpha) = [2/\Gamma(\alpha)]\int_0^\infty \frac{r^{2\alpha-1}}{1+r^2} F(s = 1 + r^2)\, dr \qquad (A.11d)$$

where

$$F(s) = \mathcal{L}\left\{\frac{e^\beta - 1}{\beta}\right\} = \ln[s/(1-s)]$$

Thus $J(\alpha)$ is equal to

$$J(\alpha) = [-2\alpha/\Gamma(\alpha)]\int_0^\infty \frac{r^{2\alpha-1}}{1+r^2} \ln\left(\frac{r^2}{1+r^2}\right) dr$$

which is converted by the change in variables $\nu = r^2/(1+r^2)$ to

$$J(\alpha) = -\frac{d}{d\beta}\left[\frac{1}{\Gamma(\alpha)}\int_0^1 \nu^{\alpha+\beta-1}(1-\nu)^{-\alpha}\, d\nu\right]_{\beta=0} = -\frac{1}{\Gamma(\alpha)}\frac{\pi}{\sin(\pi\alpha)}[\psi(\alpha) + \hat{\gamma}] \qquad (A.11e)$$

where $\hat{\gamma}$ is Euler's constant and ψ is the psi function. Thus, our integral $I_4'' + I_5$ is found to be

$$I_4'' + I_5 = \left(\frac{\pi}{2nl}\right)^{1/2}(-1)\left(\frac{14 + 12\ln 2}{9}\right) \qquad (A.12)$$

The last integral is very similar to I_3 and is given by

$$I_6 = \int_0^\infty \int_0^1 \frac{1}{\beta(1-t)}\left\{1 + \frac{\exp[-\beta t(1-t)]}{\beta(1+t)}\right\} dt\, dk = \left(\frac{\pi}{2nl}\right)^{1/2}\frac{2\pi}{3} \qquad (A.13)$$

Appendix B

The question of whether D_k (eq 1.1) involves a preaveraging approximation depends on whether it is used to approximate the long-time D or short-time D_0 diffusion coefficients. Dubois-Violette and de Gennes note[42] that the two do not coincide due to deformation of the chain during diffusion. If D_k is identified with D_0, there is no preaveraging correction since there is no time for large-scale fluctuations in the short-time limit. On the other hand, if D_k is identified with the long-time diffusion coefficient, the quantity actually measured experimentally, there is definitely a preaveraging approximation.[43]

The problem then is how large is the preaveraging error. Fixman[44] first estimated the error to be on the order of 2%, Akcasu[45] has estimated 8%, and Zimm[12] and Garcia de la Torre[13] et al. have estimated a 15% error for very long chains. The Zimm and Garcia de la Torre estimates appear to be in the best accord with experiment;[28] however, the question is still being actively investigated.

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$|\mathbf{R}_{ij}|^{-1}$ choice enables the treatment of $d = 1$. The boundary conditions can then be obtained to solve the interdimensional scaling and to obtain an explicit solution that eludes the $|\mathbf{R}_{ij}|^{2-d}$ method.

The dynamical renormalization group treatment[8] must employ the $|\mathbf{R}|_{ij}^{2-d}$ form in order to use the ϵ-expansion, but in the present preaveraging approximation either form is, in principle, valid for $d = 3$. The question then becomes which of the two methods gives an ϵ-expansion that is most rapidly convergent. This is easily tested by comparing the hydrodynamic radius calculated to first order in ϵ using $|\mathbf{R}_{ij}|^{-1}$ and for a non-free-draining Gaussian chain with the well-known result[2] calculated for $d = 3$.

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Long flexible Θ chains[2] almost universally are characterized by an exponent $\delta = 0.5$, implying that the relatively dense Gaussian coil screens completely the hydrodynamic interaction of the solvent field. In good solvents, a variation in δ is commonly observed between different solvents and polymers. Our RG calculation, which incorporates the effect of excluded volume into the Kirkwood theory, indicates that this variation is probably due to the *competitive* effects of expansion due to volume exclusion and draining caused by a decrease in the screening as the polymer becomes a more open structure. The theory predicts that draining of the swollen coil produces an initial decrease in δ from the swollen-chain value[24] of $\delta = 3\nu - 1 = 0.77$, $\nu(d = 3) = 0.59$. In principle, as draining is increased, $[\eta]$ passes through a minimum and $\delta \to 1$ in the free-draining limit. However, long polymers apparently always screen to a large extent, accounting for the phenomenological range of δ in good solvents $\delta \in [0.65, 0.8]$ as noted by Flory and Fox [Flory, P.; Fox, T., Jr. *J. Am. Chem. Soc.* **1951**, *73*, 1904]. Berry [Berry, G. *J. Chem. Phys.* **1967**, *46*, 1338] and Flory and Fox anticipated the latter type of draining effect but were unable to explain it even at a semiquantitative level.

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